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Synthesis, Characterization, and Structure of a Uranyl Complex with a Disulfide Ligand, Bis(di-*n*-propylammonium) Disulfidobis(di-*n*-propylthiocarbamato)dioxouranate(VI)[1]

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Olive green crystals of the title compound, $[(n\text{-}C_3H_7)_2NH_2^+]_2[UO_2((n\text{-}C_3H_7)_2NCOS)_2(S_2)]^{2-}$, are orthorhombic, space group *Pcan*, with $a = 15.326\ (6)$ Å, $b = 17.474\ (6)$ Å, $c = 14.728\ (6)$ Å, and $Z = 4$ ($d_x = 1.45$ g/cm^3). For 1833 data, $I > \sigma_I$, $R = 0.052$, and $R_w = 0.069$. The structure was revealed by single-crystal X-ray diffraction studies to consist of $[(n\text{-}C_3H_7)_2NH_2]^+$ cations and $[UO_2((n\text{-}C_3H_7)_2NCOS)_2(S_2)]^{2-}$ anions with the uranium atom at the center of an irregular hexagonal bipyramid. The uranyl oxygen atoms occupy the axial positions. The equatorial coordination plane contains the disulfide (S_2^{2-}) group bonded in a "side-on" fashion and two oxygen and two sulfur donor atoms from the monothiocarbamate ligands. Interatomic distances are S–S = 2.05 (1) Å and U–S = 2.711 (3) Å (disulfide), U–S = 2.873 (3) Å and U–O = 2.48 (1) Å (thiocarbamate), and U–O = 1.82 (1) Å (uranyl). The nitrogen atom in the dipropylammonium cation is hydrogen bonded to the uranyl oxygen atoms.

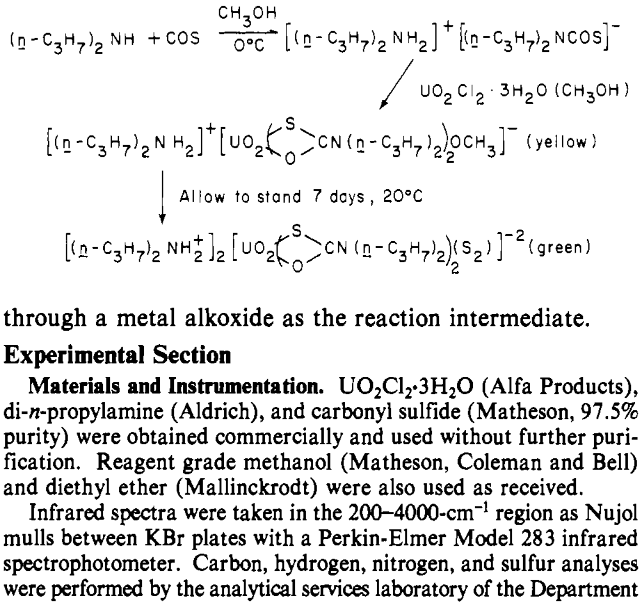
Introduction

Despite the widespread attention given metal dioxygen complexes over the last several years, the heavier congeners, metal disulfur (or disulfide) complexes,[3,4] have been relatively ignored. Several particularly interesting aspects of metal disulfide compounds are the nature of the metal–ligand bond, the synthesis of these compounds, and a comparison of their properties to the dioxygen analogues. More importantly, one can use the structurally documented members of metal disulfide compounds as spectroscopic models to correlate the spectral parameters to other disulfide complexes in order to monitor their reaction chemistry. An understanding of uranium–disulfide chemistry may be relevant to the study of those uranium compounds that are useful as desulfurization catalysts.[5,6]

A wide range of metal disulfide bonding geometries in which other ligands are attached to the same metal ion has been reported for the transition elements.[4] In the complex anion $[MoO(S_2)_2(COSCO_2)]^{2-}$, the disulfide species is bonded in a side-on manner and shared between two molybdenum metal centers.[7] Other types of metal–disulfide geometries are also exhibited in cobalt[8] and manganese[9] complexes.

The synthetic approaches usually used in introducing the S_2 unit into a metal complex include (1) a negative S_2^{2-} reagent such as found in polysulfide solutions,[10,11] (2) a positive S_2 group as is found in S_2Cl_2,[12] and (3) a neutral disulfur unit formed from molecular sulfur, S_8.[13] The preparation of the first actinide chelate–disulfide described herein represents a new synthesis of metal disulfide complexes, one which goes through a metal alkoxide as the reaction intermediate.

Scheme I. Synthesis of $[(n\text{-}C_3H_7)_2NH_2]_2[UO_2(S_2)(OSCN(C_3H_7)_2)_2]$



Experimental Section

Materials and Instrumentation. $UO_2Cl_2 \cdot 3H_2O$ (Alfa Products), di-*n*-propylamine (Aldrich), and carbonyl sulfide (Matheson, 97.5% purity) were obtained commercially and used without further purification. Reagent grade methanol (Matheson, Coleman and Bell) and diethyl ether (Mallinckrodt) were also used as received.

Infrared spectra were taken in the 200–4000-cm^{-1} region as Nujol mulls between KBr plates with a Perkin-Elmer Model 283 infrared spectrophotometer. Carbon, hydrogen, nitrogen, and sulfur analyses were performed by the analytical services laboratory of the Department of Chemistry, University of California, Berkeley.

Synthesis of $[(n\text{-}C_3H_7)_2NH_2^+]_2[UO_2((n\text{-}C_3H_7)_2NCOS)_2(S_2)]^{2-}$. The title compound is prepared by using the di-*n*-propylammonium methoxybis(di-*n*-propylthiocarbamato)dioxouranate(VI) (II) complex as the intermediate reagent. This compound is made by a procedure previously reported for it and other alkyl analogues[14-16] and then allowed to stand in situ to form the uranyl disulfide complex as shown in Scheme I. The intermediate II was prepared by bubbling carbonyl sulfide through a solution of 5 mL of di-*n*-propylamine in 10 mL of methanol in an ice bath followed by a dropwise addition with stirring of a saturated solution of $UO_2Cl_2 \cdot 3H_2O$ in methanol. After several minutes of stirring, any precipitate of the uranyl thiocarbamate methoxide (II) was filtered off, and the reaction solution containing the remaining amount of I was allowed to warm to room temperature. On standing for 1 week to ensure the completion of the reaction, dark, olive green crystals of $[(n\text{-}C_3H_7)_2NH_2^+]_2[UO_2((n\text{-}C_3H_7)_2NCOS)_2(S_2)]^{2-}$ formed. The crystals were then filtered from solution on a Büchner funnel and allowed to air-dry after being washed with petroleum ether. The compound is insoluble in such solvents as benzene and carbon tetrachloride, but it slowly dissolves in donor solvents such as dimethyl sulfoxide and dimethylformamide with apparent decomposition. On standing in the open air for several weeks, the dried complex yields a yellow mixture of decomposition products; the only

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Table I. Summary of Crystal Data and Intensity Collection

a, Å	15.326 (6)
b, Å	17.474 (6)
c, Å	14.728 (6)
V, Å^3	3944
empirical formula	$C_{26}H_{60}O_4N_4S_4U$
fw	859.08
Z	4
F(000), e	1728
d(calcd), g/cm^3	1.45
space group[a]	D_{2h}^{14}-*Pcan*
crystal shape and size, mm	needle with faces ±(110, 1$\bar{1}$0, 001) and 0.05 × 0.03 × 0.24
crystal *V*, mm^3	0.0004
temp, °C	22 ± 1
X-ray wavelength, Å	Cu Kα (λ = 1.540 56 and 1.544 39)
μ, cm^{-1}	146
transmission factor	0.37–0.65
data collection method	θ–2θ scan (1°/min along 2θ)
scan range	0.7° below Kα_1 to 0.7° above Kα_2
bkgd counts, s	10 (offset from scan limits by 0.3° of 2θ)
2θ limits, deg	4–125.6
no. of unique data	2424
unique data used (0.15 < (sin θ)/λ < 0.58, $F^2 > 0$)	2093
no. of variables	82
R (2093 data)[b]	0.051
R_w[c]	0.046
R(all data)	0.060
goodness of fit[d]	1.14

[a] General positions are ±($x, y, z; -x, y, {}^1/_2 + z; {}^1/_2 + x, {}^1/_2 + y, z; {}^1/_2 - x, {}^1/_2 - y, {}^1/_2 + z$). [b] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. [d] $R_1 = [\Sigma w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$; NO = number of data, and NV = number of variables.

Table II. Positional and Thermal Parameters with Estimated Deviations[a]

atom	*x*	*y*	*z*	B_{eq},[b] Å^2
U	0.02793 (3)	0.0	0.250	3.89
S(1)	0.0287 (2)	0.16440 (13)	0.2468 (3)	5.74
S(2)	−0.1358 (2)	0.0587 (2)	0.2513 (2)	6.45
O(1)	0.1639 (5)	0.0765 (4)	0.2513 (6)	6.45
O(2)	0.0313 (3)	−0.0010 (4)	0.1268 (4)	4.92
N(1)	0.1985 (7)	0.2014 (5)	0.253 (1)	7.16
N(2)	−0.0811 (6)	−0.0961 (5)	0.0130 (6)	5.39
C(1)	0.1394 (7)	0.1448 (6)	0.246 (1)	6.04
C(2)	0.1732 (9)	0.2829 (7)	0.267 (1)	7.20
C(3)	0.164 (1)	0.322 (1)	0.169 (1)	10.97
C(4)	0.122 (1)	0.405 (1)	0.184 (1)	12.52
C(5)	0.2914 (9)	0.1805 (9)	0.260 (1)	8.63
C(6)	0.321 (1)	0.1625 (8)	0.363 (1)	9.54
C(7)	0.418 (1)	0.135 (1)	0.358 (2)	14.35
C(8)	−0.0340 (8)	−0.1718 (7)	0.0051 (7)	5.20
C(9)	0.0670 (7)	−0.1543 (7)	−0.002 (1)	6.72
C(10)	0.1108 (9)	−0.2359 (8)	−0.0155 (9)	8.66
C(11)	−0.1772 (8)	−0.1083 (7)	0.0050 (8)	6.97
C(12)	−0.2259 (8)	−0.0315 (8)	0.0037 (9)	7.49
C(13)	−0.3280 (9)	−0.047 (1)	−0.008 (1)	10.51

[a] Here and in subsequent tables the numbers in parentheses are the estimated standard deviations for the least significant figures. [b] $B_{eq} = {}^1/_3 \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table III. Interatomic Distances (Å)

U–2 S(1)	2.873 (2)	N(2)–C(8)	1.51 (2)
U–2 S(2)	2.711 (3)	N(2)–O(2)	2.92 (2)
U–2 O(1)	2.476 (6)	N(2)–O(2)[a]	2.78 (2)
U–2 O(2)	1.815 (6)	C(2)–C(3)	1.61 (1)
S(1)–C(1)	1.73 (1)	C(3)–C(4)	1.61 (3)
S(2)–S(2)	2.05 (1)	C(5)–C(6)	1.60 (3)
O(1)–C(1)	1.25 (1)	C(6)–C(7)	1.58 (3)
N(1)–C(1)	1.35 (2)	C(8)–C(9)	1.58 (2)
N(1)–C(5)	1.47 (2)	C(9)–C(10)	1.59 (2)
N(1)–C(2)	1.49 (2)	C(11)–C(12)	1.54 (2)
N(2)–C(11)	1.49 (2)	C(12)–C(13)	1.60 (2)

[a] Atom at $\bar{x}, \bar{y}, \bar{z}$.

Table IV. Selected Angles (Deg)

S(2)–U–S(2)	44.5 (2)	C(1)–N(1)–C(2)	123 (1)
S(1)–U–O(1)	57.1 (2)	C(1)–N(1)–C(5)	118 (1)
O(1)–U–O(1)[a]	65.4 (4)	C(2)–N(1)–C(5)	119 (1)
S(1)–U–S(2)	68.0 (1)	N(1)–C(2)–C(3)	108 (1)
O(2)–U–S(1)	89.6 (3)	N(1)–C(5)–C(6)	112 (2)
O(2)–U–S(1)[a]	90.4 (3)	C(2)–C(3)–C(4)	107 (2)
O(2)–U–S(2)	92.1 (3)	C(5)–C(6)–C(7)	106 (2)
O(2)–U–S(2)[a]	90.9 (3)	O(2)–N(2)–O(2)	85.2 (3)
O(2)–U–O(1)	89.4 (3)	C(8)–N(2)–C(11)	110 (1)
O(2)–U–O(1)[a]	87.9 (3)	N(2)–C(8)–C(9)	108 (1)
O(2)–U–O(2)[a]	176.8 (4)	N(2)–C(11)–C(12)	111 (1)
S(1)–C(1)–O(1)	119 (1)	C(8)–C(9)–C(10)	104 (1)
O(1)–C(1)–N(1)	120 (1)	C(11)–C(12)–C(13)	109 (2)
S(1)–C(1)–N(1)	121 (1)		

[a] Atom at $x, \bar{y}\ {}^1/_2 - z$.

one of these products identified was sulfur. Anal. Calcd for $[n\text{-}C_3H_7)_2NH_2^+]_2[UO_2((n\text{-}C_3H_7)_2NCOS)_2(S_2)]^{2-}$: C, 36.35; H, 6.98; N, 6.52; S, 14.93. Found: C, 36.42; H, 6.87; N, 6.58; S, 14.89.

Crystallographic Data Collection and Structure Refinement. A preliminary study of the crystals was done using Weissenberg photography to establish the crystal symmetry and obtain rough cell dimensions. A fresh, green needle-shaped crystal was glued to a glass fiber and placed on a Picker FACS-I automatic diffractometer equipped with graphite-monochromated Cu Kα radiation. The cell dimensions were obtained by a least-squares procedure that used the setting angles of 12 manually centered (on Kα_1) reflections (90° < 2θ < 99°). The details of the data collection are given in Table I. ω scans of reflections 600, 060, 006 had widths at half-peak height of 0.13, 0.12, and 0.11°, respectively. A total of 6075 scans, including standards, were obtained. The three reflections, 600, 060, and 006, were measured after each 200th scan to monitor crystal decay and alignment. Crystal decay was somewhat severe, and at the end of 7 days of data collection, all three standards had diminished to 50% of their original intensities. The data were adjusted accordingly.

Absorption corrections were calculated with an analytical algorithm.[17] Azimuthal scans of integrated intensities were performed for 11 reflections in as diverse a region of reciprocal space as the instrument would allow, and the crystal dimensions were adjusted to give the best consistency of corrected intensities for these scans. The data were processed, averaged, and given estimated standard deviations by using formulas presented in the supplementary material. The factor $p = 0.05$ was used in the calculation of $\sigma(F^2)$.

From the strong pseudo-C centered pattern of the data, the uranium atom position was deduced to be on a twofold axis in the special 4c positions with coordinates $x, 0, {}^1/_4$. A three-dimensional Patterson function revealed the *x* parameter of the uranium atom as well as the positions of four other atoms. An electron density map based on the phases obtained from a least-squares refinement of those five atoms revealed seven more atoms, and the subsequent refinement and Fourier calculations revealed all 22 atoms in the final structure. Least-squares refinement converged quickly to the final structure; the maximum shift of any parameter was less than 0.2 σ in the last cycle of least squares. All of the atoms were refined with anisotropic temperature factors. A difference Fourier map showed peaks 2.2 e/Å^3 or less. Hydrogen atoms were not located in the map and were not included in the structure refinements. Because of some large discrepancies in the low-angle data, all 57 reflections below (sin θ)/λ of 0.15 were zero weighted.

The full-matrix least-squares program used minimizes the function $\sum w(\Delta F)^2 / \sum w F_o^2$. Scattering factors from ref 18 were used, and anomalous dispersion[18] corrections were applied; for *U*, $f' = -5.359$ e and $f'' = 13.409$ e.

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Table V. Infrared Data for $[(n\text{-}C_3H_7)_2NH_2^+]_2[UO_2((n\text{-}C_3H_7)_2(S_2)^{2-}]$ and $[(n\text{-}C_3H_7)_2NH_2^+][UO_2((n\text{-}C_3H_7)_2NCOS)_2OCH_3^-]$

compd	ν(U-O)[a]	ν(U-O)[b]	ν(U-O)[c]	ν(C-N), ν(C-O)	ν(C-S)	ν(S-S)
$[(n\text{-}C_3H_7)_2NH_2^+]_2[UO_2((n\text{-}C_3H_7)_2NCOS)_2(S_2)^{2-}]$ (I)	895 m, 890 m	440 m		1510 s	680 w	530 m, 520 s, 510 s
$[(n\text{-}C_3H_7)_2NH_2^+][UO_2((n\text{-}C_3H_7)_2NCOS)_2OCH_3^-]$ (II)	890 sh, 880 vs	450 s	388 s	1510 s	670 s	

[a] Asymmetric ν_3(U-O) mode of UO_2^{2+} ion. [b] Thiocarbamate U-O mode. [c] Alkoxide U-O mode.

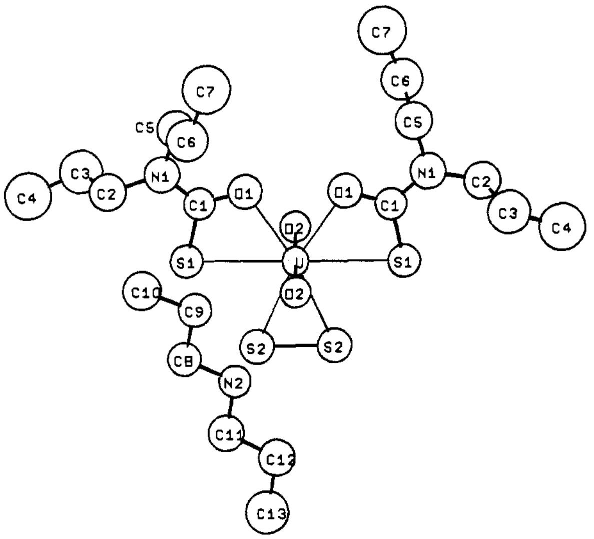

Figure 1. ORTEP drawing of the structure of $[(n\text{-}C_3H_7)_2NH_2]_2[UO_2(S_2)(OSCN(C_3H_7)_2)_2]$.

Final positional and thermal parameters are given in Table II. Distances and angles are given in Tables III and IV, and a drawing of the structure to indicate the numbering scheme is given in Figure 1. A list of anisotropic thermal parameters and observed structure factors are presented in the supplementary material.

Results and Discussion

The uranyl complex anion consists of an irregular hexagonal bipyramid centered on the uranium atom with the uranyl oxygen atoms occupying the apices (Figure 1). The six equatorial coordination positions are filled by two oxygen and two sulfur atoms from the two bidentate *n*-propylthiocarbamate ligands and two sulfur atoms from the disulfide ligand. This is in contrast to the two previously determined structures of uranyl thiocarbamates in which the uranyl ion has five equatorial ligands, only two of which are the larger sulfur atoms. The largest deviation of uranium and these six neighbors from a common plane is 0.03 Å. The two oxygen atoms of each uranyl ion are hydrogen bonded to nitrogen atoms in separate ammonium cations to form an infinite chain of anions and cations. The two N(2)-H-O(2) hydrogen bond distances are 2.78 and 2.98 Å.

The bond angles and distances in the thiocarbamate ligand in the disulfide complex are virtually identical with those in this same ligand in the related ethoxybis(di-*n*-propylthiocarbamato)dioxouranate(VI) complex previously reported;[16] the O(1)-C(1)-S(1) angle in the disulfide complex, for example, is 119°, while this same angle in the corresponding (di-*n*-propylthiocarbamato)uranyl alkoxide is 120°. These values are well within the range of 117-124° reported for this same angle in a series of metal thioacetate salts.[19,20]

A noteworthy feature of the complex is the disulfide ligand which is bonded in a "side-on" fashion to the central uranium atom. The uranium-sulfur bond distance involving the disulfide group is 2.711 Å, shorter than the 2.873-Å bond between uranium and the sulfur atom in the thiocarbamate ligand. The sulfur-sulfur distance is 2.05 Å; this compares favorably to 2.05 Å in the $[Mo_4(NO)_4S_{13}]^{4-}$ anion,[21] 2.04 Å in $[SCo_3(CO)_7]_2S_2$,[8] 2.04 Å in monoclinic sulfur,[22] 2.06-2.16 Å in the pyrite-type structures MS_2 (M = Fe, Co, Ni, Mn, and Ru),[23] and 2.05 Å for S_2Cl_2[24] and S_2H_2.[25]

Other structural comparisons between the previously reported tris(dithiocarbamato) complex $[(CH_3)_4N^+][UO_2((C_2H_5)_2NCS_2)_3^-]$[26] and the present disulfide compound reveal marked differences. The former complex consists of a US_6 equatorial coordination plane in which the six sulfur atoms are not coplanar but instead are staggered with respect to a plane perpendicular to the uranyl axis. The nonplanar arrangement can be attributed to steric factors. The uranyl disulfide compound, however, contains a S_4O_2 equatorial set of atoms which lie in a plane perpendicular to the uranyl axis; this is the same situation as is found in the triperoxouranyl compound which is comprised of a UO_6 equatorial coordination set.[27] The S(1)···S(2) interligand distance in the equatorial plane is 3.126 Å. This distance is quite similar to the S···S interligand distance of 3.07 Å observed in the sulfidotris(*N*,*N*-diethyldithiocarbamato)tantalum(V) complex[28] and shorter than the S···S interligand approach of 3.411 Å found in adjacent dithioacetate group sulfur atoms in the bis(dithioacetato)dioxo(triphenylphosphine oxide)uranium(VI) complex.[29] While all these distances are less than the sum of the van der Waals radii of 3.7 Å, there is no detectable influence on the equatorial set of oxygen and sulfur atoms which retain their planarity perpendicular to the uranyl axis.

Infrared data for the uranyl disulfide complex and the intermediate parent uranyl monothiocarbamate alkoxide are presented in Table V. Vibrational modes attributable to the linear uranyl ion are difficult to assign, partially due to the hydrogen bonding associated with this species. A strongly intense band at 880 cm^{-1}, along with a shoulder of moderate intensity at 890 cm^{-1}, can be assigned as the asymmetric ν_3 uranyl frequency in the parent thiocarbamate alkoxide on the basis of the intensities. The normal region of the infrared spectrum for this vibrational mode is ~900-950 cm^{-1}, but the hydrogen bonding in which the UO_2^{2+} species participates in these complexes presumably shifts these bands to lower frequencies. An alternate choice for this mode, with the assumption that the hydrogen bonding attenuates the absorption of this band rather than shifting it to lower wavenumber, is the medium intensity band at 915 cm^{-1}. In the case of the uranyl disulfide complex, two bands of medium intensity at 895 and 890 cm^{-1} are assigned to this vibrational mode. These assignments are in agreement with those previously made for other uranyl complexes.[30-32]

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Frequencies attributable to the thiocarbamate ligand either remain unchanged or changed only slightly upon substitution of the disulfide ligand for the methoxide ligand in the parent compound. The characteristically strong infrared band assigned as the ν(C⥲N) stretching frequency at 1510 cm^{-1} remains unchanged, while the ν(C–S) band diminished in intensity and increased in frequency by 10 cm^{-1} to a value of 680 cm^{-1}.

The uranium–oxygen (monothiocarbamate oxygen) band had been reported at 455 cm^{-1} in the infrared spectrum of $U((C_2H_5)_2NCOS)_4$,[33] comparing quite favorably with the 440 and 450-cm^{-1} values observed here for the uranyl thiocarbamate disulfide and its thiocarbamate alkoxide parent compound, respectively. The uranium–oxygen (alkoxide oxygen) stretching frequency is found at 388 cm^{-1} in the parent uranyl alkoxide compound, a value identical with that tabulated for terminal uranium–oxygen and bridging uranium–oxygen vibrations for uranium(IV) and uranium(VI) alkoxides, respectively.[34] This assignment is further corroborated when one replaces OCH_3^- in $[(n\text{-}C_3H_7)_2NH_2^+][UO_2((n\text{-}C_3H_7)_2NCOS)_2OCH_3^-]$ with the S_2^{2-} ligand; the band at 388 cm^{-1} in the original thiocarbamate alkoxide disappears, while all other bands in that region are left unchanged.

The sulfur–sulfur stretching frequency in other metal disulfide complexes has been reported to lie in the ~500–530-cm^{-1} region.[35] In the spectrum of the uranyl thiocarbamate disulfide described here, a triplet set of bands appears at 510, 520, and 530 cm^{-1}, which can be assigned as the ν(S–S) stretching frequencies. This assignment is in excellent agreement with the triplet set of bands assigned to the ν(S–S) of the $[Mo_4(NO)_4S_{13}]^{4-}$ anion.[21] This vibrational mode is often strongly coupled, as has been experimentally shown by Muller and co-workers using ^{92}Mo and ^{100}Mo isotopic substitution in the study of the $[Mo_3S(S_2)_6]^{2-}$ complex anion.[4]

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Supplementary Material Available: Listings of data processing formulas, anisotropic thermal parameters, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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The Heteropolyvanadate of Phosphorus. Crystallographic and NMR Studies[1]

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The guanidinium salt of 14-vanadophosphate, $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$, was isolated by treating the mixture of $NaVO_3$ and H_3PO_4 (V:P ≈ 4, pH 2–3) with excess guanidine hydrochloride. Crystal data: tetragonal, space group $I\bar{4}$; $a = 13.058$ (2), $c = 18.431$ (6) Å; $Z = 2$. The structure was refined by using 2257 independent reflections to a conventional weighted R factor of 0.062. In the anion twelve V atoms form the usual Keggin structure and the remaining two V atoms occupy the pits on the Keggin molecule where a $\bar{4}$ axis is passing, forming trigonal-bipyramidal caps. Such a "bicapped Keggin" structure has never been observed in heteropolyanions of Mo and W. ^{31}P and ^{51}V NMR spectra of the aqueous solutions of the 1:14 bicapped Keggin anion showed a single ^{31}P resonance and two broad ^{51}V resonances with an intensity ratio of 2:12 (assigned to the capping 5-coordinated V atoms and the 6-coordinated V atoms in the Keggin units, respectively). The pH dependence of ^{31}P and ^{51}V chemical shift values could be explained by the protonation of the 1:14 anion. NMR studies of the NaH_2PO_4–$NaVO_3$–H_2SO_4 aqueous system ($^1/_2 \leq$ V:P ≤ 14, $1 <$ pH < 6) at room temperature revealed that the 1:14 vanadophosphate anion exists in a wide range of V:P ratios as the only detectable heteropolyanion in this system.

Introduction

A number of heteropolymolybdates and -tungstates, including polyanions where some of the molybdenum or tungsten atoms are replaced by vanadium atoms, have been subjected to extensive studies. But, our knowledge about heteropolyvanadates, particularly those containing a tetrahedrally coordinated heteroatom(s), is still limited.[2] In the case of phosphorus as the heteroatoms(s), there have been several reports of the preparation of $PV_{12}O_{36}^{7-}$ anion and its protonated forms,[3] but the existence of this anion was doubted by Preuss and Schug. Instead, they claimed to have characterized 1:13 and 1:14 vanadophosphates by chemical analyses and the ultracentrifuge technique.[4] None of these previous works revealed the structure of these vanadophosphate anions and the equilibrium of solute species in the solution. In the present work, the vanadophosphate anion is investigated by X-ray crystallography and nuclear magnetic resonance spectroscopy.

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